

**Carbon nanostructures and process for the production of carbon-based
nanotubes, nanofibres and nanostructures**

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Field of the invention

The invention relates to a process for the economical and continuous production of carbon-based nanotubes, nanofibres and nanostructures. The invention also
10 relates to novel carbon nanostructures.

Brief description of the Prior Art

Carbon fibres have long been known and many methods for their production have
15 been developed, see for example M. S. Dresselhaus, G. Dresselhaus, K. Sugihara;
I. L. Spain, and H. A. Goldberg, Graphite Fibers and Filaments, Springer-Verlag,
new York (1988).

Short (micron) lengths of forms of fullerene fibres have recently been found on
20 the end of graphite electrodes used to form a carbon arc, see T. W. Ebbesen and P.
M. Ajayan, "Large Scale Synthesis of Carbon Nanotubes." Nature Vol. 358, pp.
220-222 (1992), and M. S. Dresselhaus, "Down the Straight and Narrow," Nature,
Vol. 358, pp. 195-196, (16. Jul. 1992), and references therein. Carbon nanotubes
(also referred to as carbon fibrils) are seamless tubes of graphite sheets with full
25 fullerene caps which were first discovered as multi-layer concentric tubes or
multi-wall carbon nanotubes and subsequently as single-wall carbon nanotubes in
the presence of transition metal catalysts. Carbon nanotubes have shown promis-

ing applications including nano-scale electronic devices, high strength materials, electronic field emission, tips for scanning probe microscopy, gas storage.

Presently, there are four main approaches for synthesis of carbon nanotubes. These include the laser ablation of carbon (Thess, A. et al., Science 273, 483 (1996)), the electric arc discharge of graphite rod (Journet, C. et al., Nature 388, 756 (1997)), the chemical vapour deposition of hydrocarbons (Ivanov, V. et al., Chem. Phys. Lett. 223, 329 (1994); Li A. et al., Science 274, 1701 (1996)) and the solar method (Fields; Clark L et al., US patent 6,077,401).

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The production of multi-wall carbon nanotubes by catalytic hydrocarbon cracking is described in U.S. Pat. No. 5,578,543. The production of single-wall carbon nanotubes has been described by laser techniques (Rinzler, A. G. et al., Appl. Phys. A. 67, 29 (1998)), arc techniques (Haffner, J. H. et al., Chem. Phys. Lett. 296, 195 (1998)).

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Unlike the laser, arc and solar techniques, carbon vapour deposition over transition metal catalysts has been found to create multi-wall carbon nanotubes as a main product instead of single-wall carbon nanotubes. However, there has been some success reported in producing single-wall carbon nanotubes from the catalytic hydrocarbon cracking process. Dai et al. (Dai, H. et al., Chem. Phys. Lett. 260, 471 (1996)) demonstrate web-like single-wall carbon nanotubes resulting from decomposition of carbon monoxide (CO).

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In PCT/EP94/00321 a process for the conversion of carbon in a plasma gas is described. Fullerenes can be produced by this process.

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The availability of these carbon nanotubes in quantities necessary for practical technology is problematic. Large scale processes for the production of high quality carbon nanotubes are needed. Furthermore, carbon nanostructures with closely reproducible shapes and sizes constitute another object of this invention

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DETAILED DESCRIPTION OF THE INVENTION

5 The invention and improvement we will describe now presents the improvements of the process necessary for the production of carbon-based nanotubes, nanofibres and novel nanostructures. According to the present invention, a method for producing carbon nanotubes is provided which avoids the defects and disadvantages of the prior art.

10 The invention is defined in the independent claims. Preferred embodiments are shown in the dependent claims.

In accordance with a first embodiment of the invention, there is provided a continuous process for the production of carbon-based nanotubes, nanofibres and nanostructures. This process involves the following steps preferably in that sequence.

A plasma is generated with electrical energy.

20 A carbon precursor and/or one or more catalysers or catalysts and/or a carrier plasma gas is introduced into a reaction zone. This reaction zone is in an airtight high temperature resistant vessel optionally, in some embodiments preferably having a thermal insulation lining.

25 The carbon precursor is vaporized at very high temperatures in this vessel, preferably at a temperature of 4000°C and higher.

The carrier plasma gas, the vaporized carbon precursor and the catalyser are guided through a nozzle, whose diameter is narrowing in the direction of the plasma gas flow.

The carrier plasma gas, the carbon precursor vaporized and the catalyser are guided through the nozzle into a quenching zone for nucleation, growing and quenching. This quenching zone is operated with flow conditions generated by aerodynamic and electromagnetic forces, so that no significant recirculation of feedstocks or products from the quenching zone into the reaction zone occurs.

The gas temperature in the quenching zone is controlled between about 4000°C in the upper part of this zone and about 50°C in the lower part of this zone.

The carbon-based nanotubes, nanofibres and other nanostructures are extracted following the quenching. The quenching velocity is preferably controlled between 10^3 K/s and 10^6 K/s (K/s degrees Kelvin per second).

Finally, the carbon-based nanotubes, nanofibres and nanostructures are separated from other reaction products.

The plasma is generated in the preferred embodiment of this invention by directing a plasma gas through an electric arc, preferably a compound arc created by at least two, preferably three electrodes.

Further preferred features of the claimed process which can be used individually or in any combination encompass the following:

- The plasma is generated by electrodes consisting of graphite.
- The arc is generated by connecting an AC power source to electrodes, preferably one where the current frequency lies between 50 Hz and 10 kHz.
- The absolute pressure in the reactor lies between 0.1 bar and 30 bar.
- The nozzle used consists of graphite at its inner surface.
- The nozzle is formed as a continuous or stepped cone.

- The nozzle used has a downstream end which abruptly expands from the nozzle throat.
- The carbon precursor used is a solid carbon material, comprising one or more of the following materials: Carbon black, acetylene black, thermal black, graphite, coke, plasma carbon nanostructures, pyrolytic carbon, carbon aerogel, activated carbon or any other solid carbon material.
- The carbon precursor used is a hydrocarbon preferably consisting of one or more of the following: methane, ethane, ethylene, acetylene, propane, propylene, heavy oil, waste oil, pyrolysis fuel oil or any other liquid carbon material.
- Solid catalyst is used consisting of one or more of the following materials: Ni, Co, Y, La, Gd, B, Fe, Cu is introduced in the reaction zone.
- A liquid catalyst is used consisting of one or more of the following materials: Ni, Co, Y, La, Gd, B, Fe, Cu in a liquid suspension or as a corresponding organometallic compound which is preferably added to the carbon precursor and/or to the carrier gas.
- A gas carrying a carbon precursor and/or carrying catalyst and/or to produce the plasma and/or to quench the products and/or to extract the products comprises or consists of one or more of the following gases: Hydrogen, nitrogen, argon, carbon monoxide, helium or any other pure gas without carbon affinity and which is preferably oxygen free.
- The gas temperature in the reaction zone is higher than 4000°C.
- The gas temperature in the quenching zone is controlled between 4000°C in the upper part of this zone and 50°C in the lower part of this zone.
- The carrier plasma gas flow rate is adjusted, depending on the nature of the carrier plasma gas and the electrical power, between 0.001 Nm³/h to 0.3 Nm³/h per kW of electric power used in the plasma arc.
- The quenching gas flow rate is adjusted, depending on the nature of the quenching gas, between 1 Nm³/h and 10 000 Nm³/h.
- A portion of the off-gas from the reaction is recycled as at least a portion of the gas for generating the plasma.

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- A portion of the off-gas from the reaction is recycled as at least a portion of the gas for generating the quenching gas.
 - A carbon precursor is injected through at least one injector, preferably through two to five injectors.
 - 5 • A carbon precursor is injected into the reaction zone.
 - A carbon precursor is injected with a tangential and/or with a radial and/or with an axial flow component into the reaction zone.
 - A catalyst is injected into the reaction zone and/or the quenching zone.
 - The process is carried out in the total absence of oxygen or in the presence of
10 a small quantity of oxygen, preferably at an atomic ratio oxygen/carbon of less than 1/1000.
 - If the plasma gas is carbon monoxide, the process is carried out in the presence of oxygen with a maximum atomic ratio oxygen/carbon of less than 1001/1000 in the plasma gas.
 - 15 • One or more of the following products is recovered.
 - i. Carbon black
 - ii. Fullerenes
 - iii. Single wall nanotubes
 - 20 iv. Multi-wall nanotubes
 - v. Carbon fibres
 - vi. Carbon nanostructures
 - vii. Catalyst
- 25 A yet further embodiment of this invention is a reactor to carry out the process of this invention. This reactor comprises in open flow communication
- A head section comprising
- 30 i. at least two, preferably three electrodes
 - ii. a carbon precursor supply and/or a catalyst supply and/or a gas supply.

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- At least one injector for carbon precursor and/or catalyst injection into the reaction zone,
- 5 - a reaction zone designed in size, shape and choice of materials so that the gas temperature during operation is 4000°C or higher, preferably is well above 4000°C,
- 10 - a quenching zone designed in size, shape and choice of materials so that the gas temperature is controllable between 4000°C in the upper part of this zone and 50°C in the lower part of this zone,
- 15 - a nozzle shaped choke, narrowing the open flow communication direction between the reaction zone and the quenching zone.

15 The electrodes are connected to means for creating an electric arc between the electrodes when a sufficient electric power is supplied. Thereby, an arc zone is generated into which the gas from the gas supply can be fed to generate a plasma gas and in which the carbon precursor can be heated at a vaporization temperature
20 of 4000°C and higher, preferably well above 4000°C.

25 The reactor in its preferred structure has substantially an interior cylindrical shape. Typically and preferably the reactor at the surfaces exposed to high temperatures is from graphite or respectively graphite containing high temperature resistant material. The reactor in the preferred embodiment comprises a chamber with a
30 height between 0.5 and 5 m and a diameter between 5 and 150 cm.

30 In a more specific embodiment the reactor of this invention comprises temperature control means for the quench zone. These temperature control means are particularly selected from thermal insulating lining, fluid flow, preferably water flow,

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indirect heat exchange means and flow and/or temperature controlled quench gas injection means.

The nozzle mentioned is in the preferred embodiment a tapering choke followed
5 by an abruptly expanding section.

In accordance with a yet further embodiment of the invention, there are provided novel carbon nanostructures. These carbon nanostructures have the shape of a linear, i.e. essentially un-branched chain of connected and substantially identical
10 sections of beads, namely spheres or bulb-like units or trumpet shaped units. These trumpet shaped units form carbon nanostructures the SEM or TEM of which resembles a necklace-like structure. These novel carbon nanostructures preferably have diameters of the spherical portions of the spheres or bulb-like units or respectively of the large end of the trumpet shaped units in the range of
15 100 to 200 nm. The shapes mentioned are those visible in TEM at very large magnification and in HRTEM.

The carbon nanostructures of this embodiment of the invention are connected to fairly long chains and as a rule all of these chains have at least 5 beads connected
20 to each other. The structures will preferably have 20 to 50 beads in one chain.

In yet another variation of the carbon nanostructures of this invention, these are filled or at least substantially filled with catalyst metal, more specifically with nickel or nickel/cobalt. These metal filled nanostructures form an excellent source
25 of catalyst for the process to produce such nanostructures. Separating these structures from the product of the quenching zone and introducing the structures back into the reaction zone is a recirculation of the catalytic material in an encapsulated and finely divided form. In the reaction zone itself, the carbon and the metal are both evaporated.

In one embodiment the bulb-like structures of the inventive carbon nanostructures are connected together at the neck portion.

Preferred applications of these new nanostructures:

- 5 The present carbon nanotubes are different in shape when compared to the conventional multi-wall nanotubes which exhibit a perfect stacking of graphitic cylinders. In that sense, the described novel structures, in particular such bamboo-shaped structures have advantages e.g. in gas storage (easier way to store hydrogen between the graphitic cones), and also for field emission properties, which are
10 known to depend on the topology at the nanotube tip apex, and more specifically to the conical angle (related to the number of pentagons present at the tip apex).

On the other hand, the necklace-like nano-structures have never been reported before, and they allow in a preferred embodiment the combination in composite
15 materials both when incorporated into the matrix in an oriented or in a non-oriented way. A preferred embodiment of the invention is thus a composite comprising the necklace-like nano-structures in a matrix, preferably a polymer matrix. Such nano-objects increase the interaction between the nano-fiber and the host material, as compared to conventional tubes. They increase the mechanical prop-
20 erties of composite materials. As the nano-spheres are intrinsically connected, and can contain metal catalyst, these nano-necklaces can also be used in nano-electronics.

The invention will be further illustrated, preferred details and combination of de-
25 tails of the invention shown in conjunction with examples and the drawing in which:

Figure 1 shows a schematic view of a facility or an apparatus for carrying out the process of the invention.

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Figure 2 shows a variation of an apparatus of Figure 1.

Figure 3 shows a yet further variation with some added specific features of an apparatus in accordance with the invention.

5 Figure 4 shows a SEM picture of open multi-wall nanotubes.

Figure 5 shows a SEM image of a spaghetti-like arrangement of multi-wall and necklace-shaped nanotubes.

10 Figure 6 shows a TEM picture of necklace shaped carbon nanostructures in accordance with the invention.

Figure 7 shows a HRTEM picture of carbon necklace structures of bulb-like beads.

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Figure 8 shows a TEM picture of carbon nanotubes having a bamboo-like structure.

Figure 9 shows a HRTEM picture of single-wall nanotubes.

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The reactor 1 is designed in a way that it consists of two different but adjacent zones. Zone A, for the vaporization of the precursor (carbonaceous products and catalytic products), is maintained at a very high temperature due to the action of a thermal plasma and an appropriate thermal insulation. Zone B, for the nucleation and maturation of the carbon-based nanostructures, is kept between 4000°C in the upper part and less than 50°C in the lower part due to an adequate thermal insulation.

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In zone A, the geometry of the internal fittings has the shape of a venturi which is specifically designed to assure the complete vaporization of the precursors. Each of the three electrodes 3, of which only two are shown in Figure 1, is connected to

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one of the three phases of an electric three-phase generator and supplied with alternative current. After activation of the electric generator and the establishment of the plasma by the contact of the three electrodes, the electrodes are automatically drawn apart and a plasma flow is established in zone A of the reactor, which
5 allows the complete vaporization of the precursor. Once the plasma is established, the control of the electrodes to compensate for their erosion is effectuated automatically. Together with a carrier plasma gas, the carbonaceous product and the catalytic product are continuously injected into zone A of the reactor, for example in 4.

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The electric power source is of the type "three-phase", whereby the frequency of the supply can vary between 50 Hz and 10 kHz. Each of the three phases of the electric source is connected to one of the three electrodes of the reactor. The inventors discovered that an increase of the frequency of the electric supply beyond
15 50 Hz, which can range from 50 Hz to 10 kHz, achieves particular advantages. This increase of the frequency allows on the one hand an increase in the stability of the plasma, and on the other hand a very advantageous increase in the homogeneity of the mixture of the plasma gas with the carbonaceous product vaporized and the catalyst product due to important turbulence phenomena in the flow field
20 of zone A. This turbulence is caused by the combined effects of arc rotation between the three electrodes successively changing from anode and cathode with current frequency and the electromagnetic forces induced by the current in the electrodes and the arcs themselves.

25 In zone B of the reactor, the zone of the nucleation and growing of the carbon-based nanostructures, the temperature of the flow is maintained between 4000°C in the upper part and less than 50°C in the lower part due to an adequate thermal insulation. The absolute pressure in zones A and B of the reactor can be between 100 mbar and 30 bar. Into this zone, a certain quantity of cold gas is injected in 5,
30 allowing the quenching of the aerosols and their extraction from the reactor in 6 by means of an extraction system cooled by a liquid, a gas or any other means of

refrigeration known within the state of the art. Afterwards, the aerosol is transported to a heat exchanger in 7 where it is cooled down further to a stabilization temperature of the envisaged carbon-based nanostructures and finally passes through a separation system in 8 where the carbon-based nanostructures are separated from the gas phase. Eventually, the carbon-based nanostructures are taken out in 10 by means of an airtight valve represented in 9 and the gas is vented in 11.

In accordance with a preferred embodiment of the invention, full control of the extraction conditions and the quenching rate is foreseen thereby controlling the quality of the nanostructures obtained. Both the temperature at which the aerosol is extracted and the quenching speed of the aerosol are preferably controlled to ensure high quality products.

Preferred control approaches include the following. The temperature at which the extraction is effectuated and the residence time for product maturation is controlled by the variation of the axial position of the injection point of cold gas in 5 and the extraction point in 6 in zone B. The quenching velocity rate is controlled by a variation in the nature and the flow rate of cold gas injected in 5, by the effectiveness of the extraction system cooled in 6 and by the effectiveness of the heat exchanger in 7.

In a preferred embodiment shown in Figure 2, zone B of the reactor is modified by the installation of a recirculation system for the quenching gas flow as described hereafter. In zone B of the reactor where the temperature is maintained between 4000°C in the upper part and less than 50°C in the lower part, a device cooled by a liquid, a gas or any other means of refrigeration known within the state of the art is introduced in 5, which allows the extraction of the aerosols in 6 and the transport to a separation system in 7. The temperature of the zone of which the extraction is effectuated, is controlled by the variation of the axial position of the injection point of cold gas in 11 and the extraction point in 5. The

quenching rate is controlled by a variation in the flow rate of cold gas injected into zone B in 11 by means of a blower 10, by the effectiveness of the extraction system cooled in 5 and by the effectiveness of the heat exchanger in 6. Therefore, the gas flow rate in the recirculation circuit is independent of the initial carrier gas flow entering in 4. The aerosol is transported to a heat exchanger in 6 where it is cooled down further to a stabilization temperature of the envisaged carbon-based nanostructures and finally passes through a separation system in 7 where the carbon-based nanostructures are separated from the gas phase. Eventually, the carbon-based nanostructures are taken out in 9 by means of a valve 8. The excess gas flow equivalent of the amount of gas entering in 4 is vented in 12.

In a preferred embodiment shown in Figure 3, zone B of the reactor is modified by the installation of a recirculation system for the quenching gas flow and the carrier plasma gas supplying the plasma itself as described hereafter. In zone B of the reactor where the temperature is maintained between 4000°C in the upper part and less than 50°C in the lower part, a device cooled by a liquid, a gas or any other means of refrigeration is introduced in 5, which allows the extraction of the aerosols in 6 and the transport to a separation system 7. The temperature of the zone of which the extraction is effectuated, is controlled by the variation of the axial position of the injection point of cold gas in 12 and the extraction point 5. The quenching rate is controlled by a variation in the flow rate of cold gas injected into zone B in 12 by means of a blower 10, by the effectiveness of the extraction via extraction point 5 and by the effectiveness of the heat exchanger 6. Therefore, the gas flow rate in the recirculation circuit is independent of the initial carrier gas flow entering in 18. The aerosol is transported to a heat exchanger 6 where it is cooled down further to a stabilization temperature of the envisaged carbon-based nanostructures and finally passes through a separation system 7 where the carbon-based nanostructures are separated from the gas phase. Eventually, the carbon-based nanostructures are taken out in 9 by means of a valve 8. A part of the gas vented in 13 is used as carrier plasma gas in 14. A feeding system 15 with a gas feeding 18 and a valve 16 allows the continuous feeding of solid

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carbon material in 4. The excess gas flow equivalent of the amount of gas entering in 18 is vented in 17.

5 The raw material used as a precursor consist of one or a combination of the following elements: A carbonaceous product, a catalytic product and/or a gaseous product. The product used as carbonaceous product can be of solid, liquid or gaseous nature.

10 In the case of solid carbonaceous materials, different types of products can be utilized, for example: Finely milled graphite, acetylene black, carbon black degassed, milled pyrolitic carbon, activated carbon, pyrolyzed carbon aerogels, plasma carbon nanostructures. The carbon content of the utilized carbonaceous material should be as high as possible, preferably higher than 99 weight %. The average particle size of the carbonaceous materials should be as small as possible, 15 preferably smaller than 10 μm in diameter, to ensure its complete vaporization when passing through the plasma.

In the case of liquid and gaseous carbon precursors any kind of hydrocarbon can be considered.

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The catalytic material associated with the carbonaceous material can consist of one or a mixture of elements well known for their catalytic characteristics in carbon nanotubes synthesis, such as: Ni, Co, Y, La, Gd, B, Fe, Cu. The catalytic materials are introduced in zone A (preferred) or zone B of the reactor, either in form 25 of a powder mixed with the carbon material, or in form of a deposit on the carbon material, or in form of a solid whereby the morphology can vary corresponding to the hydrodynamic prevalent in the reactor, or in the form of a liquid. The mass ratio of catalyser to carbon can vary between 0.1% and 50%.

30 In the case of liquid carbon precursors, the catalytic elements are preferably mixed with the liquid.

In the case of gaseous carbon precursors, the catalytic elements are preferably introduced in form of a powder.

- 5 In the case of solid carbon precursors, the catalytic elements are preferably introduced in form of a deposit on the carbon material.

The plasma gas is preferably a pure gas: Helium, argon, nitrogen or a mixture of one of these gases with the following gases: Helium, argon, nitrogen, carbon
10 monoxide, hydrogen.

The quenching gas can be identical to the plasma gas or consist of any kind of gas mixture.

- 15 In the following examples further preferred features, feature combinations and embodiments of this invention are illustrated.

The examples were carried out in a reactor set-up substantially as shown in Figures 1 and 2.

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Example 1:

The reactor set-up, described in Figure 1, consists of a cylindrical reactor of a height of 2 meters in stainless steel with water-cooled walls and 400 mm internal
25 diameter. The upper part of the reactor is fitted with thermal insulation cone-shaped in graphite of 500 mm height and an internal diameter between 150 and 80 mm. Three electrodes in graphite of 17 mm diameter are positioned through the head of the reactor by a sliding device system electrically insulated. A central injector of 4 mm internal diameter allows the introduction of the precursor by
30 means of a carrier plasma gas in the upper part of the reactor. A plasma power supply, employing a three phase electricity source up to 666 Hz with a maximum

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power of 263 kVA, a RMS current range of up to 600 A and a RMS voltage range of up to 500 V, was used to supply electricity to the three graphite electrodes, their tips being arranged in the shape of an inversed pyramid.

- 5 The carrier plasma gas is helium and the precursor is carbon black with a deposit of nickel - cobalt corresponding to a weight ratio in relation to the carbon of 2,5 weight % for the nickel and 3 weight % for the cobalt. The gas for the quenching is helium.
- 10 The following table gives the main operating conditions.

Nature of carrier plasma gas - flow rate	Helium - 3 Nm ³ /h
Precursor flow-rate	850 g/h
RMS Voltage	100 V
RMS Current	400 A
Frequency	666 Hz
Active power	61 kW
Average temperature in the injection zone	5200°C
Average temperature in the extraction zone	3500°C
Quenching gas flow-rate	30 Nm ³ /h
Quenching velocity (3500°C - 500°C)	10 ⁶ K/s

- More than 98% of the injected precursor mass was removed from the filter. The recovered product is composed of: 40% of Single Walled Carbon Nanotubes, 5.6% of fullerenes whereby 76% of C60 and 24% of C70, 5% of Multi Walled Carbon Nanotubes, about 20% of fullerene soots, about 30% of undefined carbon nanostructures with catalyst particles. Quantitative and qualitative measurements of carbon nanostructures are achieved using Scanning Electronic Microscopy and Transmission Electronic Microscopy. Quantitative and qualitative measurements of the fullerenes (C60 and C70) are achieved using UV - visible spectroscopy at the wavelengths 330 nm and 470 nm after Soxhlet-extraction with toluene.

Example 2

One operates in similar conditions to example 1 but according to the configuration
5 corresponding to Figure 2. Carrier plasma gas is nitrogen at a flow-rate of 2
Nm³/h. The quenching gas is nitrogen at a flow-rate of 50 Nm³/h. Electrical con-
ditions are 350 A and 200 V. In these conditions necklace shaped carbon nanos-
tructures are produced in very high concentration.

10 Example 3

One operates in similar conditions to example 1 but according to the configuration
corresponding to Figure 2. Carrier plasma gas is helium at a flow rate of 3 Nm³/h.
The quenching gas is a mixture of nitrogen/helium at a flow rate of 50 Nm³/h.
15 Electrical conditions are those of example 1. The precursor is ethylene (C₂H₄)
mixed with nickel-cobalt powders corresponding to a weight ratio in relation to
the carbon of 3 weight % for the nickel and 2 weight % for the cobalt. The recov-
ered product is composed of: 55 weight % of single walled carbon nanotubes, 13
weight % of carbon nanofibres and multi walled carbon nanotubes, the rest of
20 undefined carbon nanostructures with catalyst particles.

The carbon nanostructures of Fig. 4 - 9 illustrate embodiments of the invention.
The preferred carbon nanostructures of this invention have the structure of a linear
chain of connected, substantially identical sections of beads, namely spheres or
25 bulb-like units or trumpet shaped units, preferably having a diameter of the
spheres of the spherical section of the bulb-like units or respectively the large di-
ameter of the trumpet shaped section in the range of 100 to 200 nanometres. All
spheres or bulb-units exhibit nearly the same diameter. These periodic graphitic
nano-fibers are characterized by a repetition of multi-wall carbon spheres ('neck-
lace'-like structure), connected along one direction, and containing frequently a
30 metal particle encapsulated in their structure. The periodicity of these nanostruc-

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tures relates them to the bamboo nanotubes, but they clearly differ by their periodic necklace-like structure and the presence of these metal inclusions.